Determination of Aluminium and Sulfur in Ferromolybdenum

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Synopsis

In determining aluminium and sulfur in ferromolybdenum, iron and molybdenum were removed by methyl isobutyl ketone extraction method. After the removal of iron and molybdenum, aluminium was determined gravimetrically or volumetrically by using oxine, by which 0.1–1 per cent aluminium in ferromolybdenum could be determined. By using methyl isobutyl ketone for ether, the danger of explosion caused by organic vapour and the interference of molybdenum could be avoided. Sulfur was determined gravimetrically as barium sulfate down to 0.005 per cent content of it. The present procedure is superior in its simplicity and in being free of the obstruction by molybdenum trioxide to the usual combustion method for sulfur.

I. Introduction

To carry out the determination of aluminium and sulfur in ferromolybdenum, iron and molybdenum were removed by extraction with methyl isobutyl ketone. JIS method adopted the separation of majority of iron and molybdenum by ether extraction for the determination of aluminium in ferromolybdenum but the extraction with methyl isobutyl ketone is simpler and safer, and gives a satisfactory result.

Determination of sulfur in ferromolybdenum can be carried out in a short time by the combustion method but the value tends to become higher by contamination of molybdic acid in the SO_3 absorbent solution. Therefore, it is necessary to take special caution in adjusting the flow rate of oxygen and in filling the foot of the cap with glass wool. There is also a method of determination by combination of the combustion method with redox titration, which, however, becomes too complicated.

In the present study, the combustion method being not used, the sample was dissolved in acid, molybdenum and iron were removed by extraction with methyl isobutyl ketone, and the amounts of sulfur was determined by gravimetry. This method takes rather a long time but is not very complicated, resulting in satisfactory values.

II. Determination of aluminium

1. Reagents

Sulfuric acid, nitric acid, hydrofluoric acid: First grade reagents. Methyl

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isobutyl ketone: First grade reagents. Iron: Electrolytic iron.
Molybdenum: Sodium molybdate, First grade reagents.

2. Experimental method

The sample was decomposed with nitric, hydrofluoric, and sulfuric acids, evaporated by heating to remove hydrogen fluoride, and rendered acidic with hydrochloric acid. After majority of iron and molybdenum were removed by extraction with methyl isobutyl ketone, tartaric acid was added to the solution, and the solution was made slightly alkaline by adding ammonia water, iron (II) in the solution was reduced by addition of potassium cyanide and sodium sulfite, aluminium was precipitated by addition of oxine, and was determined by gravimetry or volumetry.

3. Extraction

Experiments were carried out to find out the optimal number of repetition times for the extraction and washing of extract solution, using a synthetic sample which contained (0.4 g of iron and 0.6 g of molybdenum), and the results obtained are listed in Table 1. As clearly seen in this table, twice extractions

Table 1. Times of extraction.

Al added (mg)	Al found (mg)	(%)	Error (mg)	(%)	Remark
5.96	5.92	0.592	−0.04	−0.004	once extraction
	5.93	0.592	−0.03	−0.003	
	5.97	0.597	+0.01	+0.001	
	5.96	0.596	0.00	0.00	twice extraction
	5.96	0.596	0.00	0.00	
	5.93	0.593	−0.03	−0.03	
	6.00	0.600	+0.04	+0.004	twice extraction
	6.02	0.602	+0.06	+0.006	washing with
	5.95	0.595	−0.01	−0.001	8NHCl 10 mL

(Fe taken 0.4 g, Mo taken 0.6 g)

are sufficient. In this case, the addition of hydrofluoric acid in a platinum dish was omitted and the sample solution with nitric and sulfuric acids in the beaker, was evaporated until white fumes came out. Other procedures were the same as those used for the treatment of the sample.

The same experiment was carried out by varying the amount of aluminium added. Some ferromolybdenum samples contained around 1 per cent of copper. Then the experiment was also done in the solution containing 20 mg of copper. These results are shown in Table 2.

It was found from these experiments that it was possible to determine aluminium in a range of 0.1～1 per cent.

4. Determination procedure

1g of the sample is placed in a platinum dish, 20 ml of nitric acid (1+1) is added, hydrofluoric acid is added in drops to accelerate the decomposition of sample and 5 ml of sulfuric acid (1+1) is added. The mixture is heated until white

Table 2. Results of determination of Al in synthetic sample.

Al added (mg)	Al found (mg)	(%)	Error (mg)	(%)	Remark
1.19	1.18	0.118	−0.01	+0.001	
	1.24	0.124	+0.05	+0.005	
8.93	8.96	0.896	+0.03	+0.003	
	8.97	0.897	+0.04	+0.004	
5.96	5.95	0.595	−0.01	−0.001	Cu 20 mg added
	5.89	0.589	−0.06	−0.006	

(Fe taken 0.4 g, Mo taken 0.6 g)

fume evolves to remove hydrofluoric acid completely. Presence of sulfuric acid does not interfere with extraction of iron or molybdenum by methyl isobutyl ketone. Therefore, it is not necessary to evaporate sulfuric acid completely, as is required in the method using ether extraction. The residue is transferred to a separatory funnel with 13 ml of water. If it is impossible to transfer the residue to a separatory funnel with a small quantity of water, the residue should be transferred to a beaker with water, evaporated to below 10 ml and transferred to a separatory funnel graduated at 40 ml. The beaker is washed with 27 ml of hydrochloric acid, which is added to original solution in the separatory funnel, and the solution in the funnel is brought to 40 ml with water and hydrochloric acid concentration in it was 8N. (If the residue in the platinum dish, after treatment with nitric and hydrofluoric acid, is treated with hydrochloric acid, a trace of platinum may dissolve out and contaminate the precipitate of aluminium-oxine salt. It is necessary, therefore, to treat residue not with hydrochloric acid but with water alone.) This solution is shaken with 40 ml of methyl isobutyl ketone for 0.5～1 minute, the lower layer is transferred to another separatory funnel, and shaken again with 20 ml of methyl isobutyl ketone. The lower acid layer is transferred to a beaker and heated until white fumes evolve. A small quantity of nitric acid is added to this solution to ensure complete decomposition and again heated until white fumes evolve. The solution is heated with 50 ml of water, and 2 ml of nitric acid is added to oxidize iron. To this solution, 5 ml of 20 per cent tartaric acid solution is added, and neutralized by dropwise addition of ammonia water, until about 10 drops more of ammonia water is added to bring the solution to slight alkalinity. After the solution is cooled to room temperature, 2.5 ml of 20 per cent potassium cyanide solution and 5 ml of 10 per cent sodium nitrite solution are added, and the mixture is shaken thoroughly. This solution is warmed to ca. 70°C to reduce iron (III) to iron(II). Oxine solution is added to it and the solution is warmed to precipitate oxine compound of aluminium completely. This precipitate is used to determine aluminium by gravimetry or volumetry.

5. Analytical result

Results obtained by applying the foregoing analytical procedure on ferromolybdenum samples are shown in Table 3. Because of the absence of a suitable sample with known content of aluminium, experiments were carried out with samples to which aluminium was added in option.

Table 3. Results of determination of Al in ferromolybdenum.

Sample taken (g)	Al added (mg)	Al found (mg)	Al found (%)		Al calculated (mg)	Al calculated (%)	Error (mg)	Error (%)
1.00	0	0.828	0.083					
	0	0.886	0.089					
	0	0.845	0.085	0.085				
	0	0.810	0.081					
	0	0.875	0.088					
1.00	5.96	6.891	0.689		6.04	0.604	+0.08	+0.008
	〃	6.900	0.690		6.05	0.605	+0.09	+0.009
	〃	6.800	0.680		5.95	0.595	−0.01	−0.001

III. Determination of sulfur

1. Reagents

Nitric acid, potassium chlorate, and hydrochloric acid: First grade, reagents
Methyl isobutyl ketone: First grade reagents
Iron: Electrolytic iron.
Molybdenum: Sodium molybdate, First grade reagents
Zinc: First grade reagents
10 per cent aqueous solution of barium chloride: First grade reagents

2. Experimental method

The sample is treated and decomposed by nitric acid and potassium chlorate, iron and molybdenum are removed by extraction with methyl isobutyl ketone after the addition of hydrochloric acid, and the aqueous layer is evaporated. Hydrochloric acid is added to the residue and the solution is again evaporated to dryness to remove silicon. The residue is dissolved in water and hydrochloric acid, zinc is added to reduce a trace of iron (III) to iron (II), and barium chloride solution is added to precipitate barium sulfate. Sulfur is determined with this precipitate.

3. Extractions

To a synthetic sample (containing 0.4 g of iron and 0.6 g of molybdenum), a known amount of sulfur was added in the form of sulfuric acid, and the solution was extracted with methyl isobutyl ketone. As shown in Table 4, the extraction was completed by three extractions, and the loss of sulfur by this extraction was found to be negligible. Results of the determination of sulfur by extraction method, after addition of molybdenum to cast iron, are shown in Table 5. Also, in this case, the loss by extraction was not observed. Determination of sulfur added to Si-Mo and pig iron was carried out and the results are listed

Table 4. Sulfur reproducibility after extraction.

S added (g)	S found (g)	Error (g)	Remark
0.0015	0.0013	−0.0002	three times extraction
	0.0014	−0.0001	
	0.0014	−0.0001	
0.0015	0.0018	+0.0003	twice extraction
	0.0019	+0.0004	
	0.0017	+0.0002	

Table 5. Determination of cast iron.

Sample	Sample taken (g)	Mo added (g)	S found (%)
Cast iron	1.0034	0	0.0012_2
	1.0073	0	0.0012_3
	1.0012	0.600	0.0012_2
	1.0037	0.600	0.0012_5
	1.0026	1.000	0.0012_3

Table 6. Determination of silico-molybdenum and pig iron.

Sample	Sample taken (g)	Mo added (g)	S in sample (g)	S added (g)	Total S (g)	Calculated (g)
Si-Mo	0.5081	0.50	0.0000_2			
	0.5042	0.50	0.0000_2	0.0012	0.0012	0.0011_8
	0.5036	0.50	0.0000_2	0.0012	0.0012	0.0011_8
Pig iron	1.0001	0.60	0.0006_8 Av			
	1.0004	0.60	0.0006_3 0.00065			
	1.0003	0.60	0.0006_5	0.0012	0.0018	0.0011_9
	1.0008	0.60	0.0006_5	0.0012	0.0018	0.0011_3

in Table 6, which shows the excellent reproduced amounts of sulfur added.

4. Determination procedure

To 2∼5 g of a sample placed in a 500 ml beaker, 1 g of potassium chlorate and 75 ml of nitric acid (to 5 g of the sample) are added gradually, the beaker is covered with a watch glass, and heated to effect the sample decomposition. The beaker must be cooled in cold water while adding the reagents, or the reaction will occur violently. The sample solution is evaporated by heating until the precipitate of molybdic acid appears, and precipitate is dissolved by addition of 20 ml of hydrochloric acid. The cooled solution is transferred to a separatory funnel, brought to above 8N hydrochloric acidity and is with the same volume of methyl isobutyl ketone. The aqueous layer is transferred to another separatory funnel and mixed three times with methyl isobutyl ketone in the same way as in the case of iron and molybdenum. To the aqueous solution which was transferred to a beaker and evaporated, 10 ml of hydrochloric acid is added, and evaporated to dryness again. The residue is heated at 110°C for 30 minutes and cooled, and then 60 ml of hydrochloric acid (1+1) is added to it. This solution is heated to dissolve the soluble substance in the residue, and following to the

addition of 50 ml of water it is boiled for 5 minutes finally. The solution is filtered and the insoluble substances are washed thoroughly with hydrochloric acid (2+100). If the amount of sulfur is great and that of silicon is small in the sample, the amount of sample to be taken can be small and, in such a case, it is more convenient to separate silicic acid before the extraction of iron and molybdenum, with methyl isobutyl ketone. If the amount taken is large, a large amount of molybdic acid precipitate will form at the time of evaporation and the precipitate will crackle, making the further procedure difficult, in the case of which the extraction is carried out before.

This filtrate is evaporated until syrupy, 15 ml of hydrochloric acid and 30 ml of water are added, and about 2~5 g of sulfur-free granular zinc is added. The mixture is heated gently to reduce iron (III) to iron (II). The solid is filtered off and washed thoroughly with hydrochloric acid (2+100). The filtrate is diluted to about 250 ml warmed to 70°C, and 10 ml of 10 per cent barium chloride solution is added gradually. The mixture is stirred thoroughly, allowed to stand over a night, and the precipitate is collected by filtration. The precipitate on the filter paper is washed with hydrochloric acid (2+100), transferred to a platinum crucible, and ignited. The ash is weighed as barium sulfate and sulfur is determined from the following equation :

$$\text{Sulfur } (\%) = \frac{\text{BaSO}_4\,(\text{g}) \times 13.74}{\text{Sample (g)}}$$

NOTE : When the amount of silicon is large, silicomolybdic acid will be formed and this cannot be extracted completely. In such a case, the solution is brought again to 8N hydrochloric acidity, after silicon is separated, the extraction should be repeated with methyl isobutyl ketone. Alternately, the final precipitation of barium sulfate should be repeated.

Results of the determination of sulfur in ferromolybdenum sample are listed in Table 7. The samples used in these experiments were kindly donated by the Ferro-alloy Society.

Table 7. Determination of ferromolybdenum.

Sample	Sample taken (g)	S found (%)
Fe-Mo (H)	5.0010**	0.005_4
	5.0030	0.006_8
Fe-Mo (M)	2.0006	0.155_3
	2.0012	0.154_9
	2.0030	0.153_1
	2.0008	0.158_0
Fe-Mo (L)	2.0006	0.033_1
	2.0014	0.031_3
	2.0003	0.038_5
	2.0021	0.038_8

Summary

(1) For the determination of aluminium in ferromolybdenum, the separation of iron and molybdenum was effected by extraction with methyl isobutyl ketone in place of ether.

(2) Aluminium was determined by gravimetry or volumetry as oxine complex salt after removal of the main components, iron and molybdenum, by extraction with methyl isobutyl ketone.

(3) This method is simpler and safer than that by use of extraction with ether, and 0.1～1 per cent of aluminium in ferromolybdenum can be determined.

(4) The determination of sulfur in ferromolybdenum was carried out by extraction of the main components, iron and molybdenum, at 8N hydrochloric acidity, and the determination of barium sulfate by gravimetry in the usual way.

(5) This method avoids error arising from molybdic acid by combustion method, does not require any special apparatus, and comparatively simple in procedure compared with other methods.

(6) The determination of sulfur by this procedure was carried out with various kinds of ferromolybdenum samples, and it became possible to determine sulfur up to 0.005 per cent.